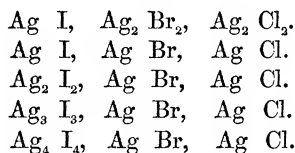


"On the Effects of Heat on some Chloro-brom-iodides of Silver."

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In a recent communication to the Society I have given the approximate coefficients of expansions of the chloride and bromide of silver, and the coefficients of contraction and expansion of the iodide of silver. It was thought that some interesting results might be obtained by alloying these bodies together, and thus forming various chloro-brom-iodides of silver, and by investigating the physical properties of such bodies and the effects of heat upon them. Accordingly these bodies were fused together in the proportions requisite to form the following compounds:—



Dr. Matthiessen ("On Alloys," Chem. Soc. Journ. 1867, p. 201) states that he believes "in nearly all cases the two metal alloys may be considered as solidified solutions of the one metal in the other;" and he continues as follows:—"By the term solidified solution I mean a solution of two substances which has been allowed to solidify, as, for instance, if a mixture of ether and alcohol were made, and sufficient cold could be produced to solidify it, we should produce a solidified solution of these two substances in one another. Again, if the chlorides of potassium and sodium, say in equal parts, be melted together and allowed to solidify, the solid thus produced is a solidified solution of the chlorides of potassium and sodium in one another. Glass is also a good example of a solidified solution; to produce it, different silicates are fused together and allowed to solidify. There is, however, an important point in the definition of the term 'solidified solution' which must not be overlooked—namely, that the components are most intimately mixed together; in fact they are homogeneously diffused in one another, and to that extent that, even in the most powerful microscope, it would not be possible to distinguish the components of a solidified solution. As examples of this fact glass may be quoted, which presents under high magnifying-power a homogeneous mass; the silver and gold in the gold-silver alloys cannot be distinguished by the same test from one another."

Accepting Dr. Matthiessen's definition, we must regard the chloro-brom-iodides of silver as solidified solutions of chloride, bromide, and

\* Read May 4, 1876. See *ante*, p. 4.

iodide of silver in one another. Such bodies are found native: *emboelite* (*ἐμβόλιον*) is a chloro-bromide of silver in which the ratio of the chloride to the bromide varies indefinitely. Minerals having respectively the composition  $\text{Ag}_3 \text{Br Cl}_2$ ,  $\text{Ag}_5 \text{Br}_2 \text{Cl}_3$ ,  $\text{Ag}_4 \text{Br}_3 \text{Cl}$ ,  $\text{Ag}_9 \text{Br}_4 \text{Cl}_5$ , and  $\text{Ag}_4 \text{Br Cl}_3$  have been analyzed by Domeyko, Field, Müller, Richter, and others. They occur chiefly in Chili, and constitute the principal ore of the silver-mines of Chañarcillo. They are described as possessing specific gravities which vary between 5·75 and 6·2; and according to Dana the colour is "greyish green, and asparagus-green to pistachio or yellowish green, and yellow; often dark, becoming darker externally on exposure." Dana further states that an iodobromide of silver is found native in Chili; but of this I am unable to find any description.

In examining the following results, we must bear in mind that we are dealing with bodies which are very differently affected by heat. For while the chloride and bromide of silver have higher coefficients of expansion than the most expansible metals (such as zinc), the iodide of silver contracts slightly when heated to a temperature of  $142^\circ \text{C}$ ., while between  $142^\circ$  and  $145^\circ\cdot5 \text{C}$ . it undergoes considerable contraction; then expands to the melting-point, undergoes considerable increase of volume in passing from the solid to the liquid condition, and expands slightly beyond this temperature and the melting-point. Moreover the iodide passes into an amorphous condition between  $142^\circ \text{C}$ . and  $145^\circ\cdot5 \text{C}$ ., and possesses a point of maximum density at  $142^\circ \text{C}$ . The following volumes are given for comparison with those of the alloys (the coefficients for both the bromide and chloride are not given because they are practically the same, and one serves for both):—

<i>Bromide of Silver.</i>		<i>Iodide of Silver.</i>		
$^\circ \text{C}$ .	Volume.	$^\circ \text{C}$ .	Volume.	
At 750 .....	= 1·167940	At 750 (liquid) .....	= 1·052946	} Contraction on cooling, expansion on heating.
380 (liquid) ...	= 1·122840	450 (liquid) .....	= 1·044990	
383 (solid) ...	= 1·048120	450 (solid).....	= 1·008659	
300 .....	= 1·038760	142 (max. density) =	1·000000	} Expansion on cooling, contraction on heating.
200 .....	= 1·027460	145·5 (aft. sudden ex.)=	1·015750	
+ 100 .....	= 1·016560	+ 70 .....	= 1·017009	
0 .....	= 1·006060	— 10 .....	= 1·017342	
— 60 .....	= 1·000000	— 60 .....	= 1·017394	

The alloys were examined in the same manner as I have previously described in determining the coefficients of expansion of their constituents\*.

They were cast into rods 8 inches long by  $\frac{1}{4}$  to  $\frac{3}{8}$  inch diameter in warm glass tubes; then by means of a fine steel saw they were cut into lengths of 6 inches, and examined in the expansion-apparatus described and

\* "On the Effects of Heat on the Chloride, Bromide, and Iodide of Silver," see *ante*, p. 280.

figured in the above-mentioned paper. The measurements were made by means of a micrometer-screw. The expansions above the point of fusion were determined by the method of the platinum cone described in the previous paper.

The alloys were made by fusing together in a porcelain crucible weighed quantities of the iodide, bromide, and chloride of silver in such proportions as furnished the five compounds described below.

1. CHLORO-BROM-IODIDE OF SILVER HAVING THE COMPOSITION  $\text{Ag I Ag}_2\text{Br}_2\text{Ag}_2\text{Cl}_2$ , OR  $\text{Ag}_6\text{I Br}_2\text{Cl}_2$ .

The alloy contains:—

Ag I ... = 26.1692	Ag .. = 60.1336
Ag Br .. = 41.8708	I .... = 14.1435
Ag Cl .. = 31.9600	Br .. = 17.8176
	Cl .. = 7.9053
<hr/>	<hr/>
100.0000	100.0000

Specific gravity 6.152, when fused and cast into rods which were allowed to cool in the air; but when the rods were allowed to cool slowly in hot paraffine, the specific gravity was found to be 6.066. The specific gravity, calculated on the assumption that no change of volume takes place, was found to be 5.836, showing a condensation equal to .0513 on the calculated volume. Fusing-point  $330^\circ\text{C}$ . Specific gravity at the fusing-point = 5.5118; at  $750^\circ\text{C}$ . = 5.057. The mass fused to a claret-red liquid, which became brick-red, dull orange, and yellow as it cooled, and when cold had a brownish-yellow colour, a good deal resembling bromide of silver. The mass contracted on solidifying, and formed a substance with crystalline fracture, not perfectly homogeneous. A small central core of less dense matter appeared near the upper end of the rod, and was formed during the contraction of the mass. The alloy gave a bright yellow powder, which turned *green* on exposure to light. Loud harsh sounds were sometimes emitted during the cooling of the mass. The substance was somewhat brittle, and broke as easily as a rod of bromide of silver of the same dimensions. Heated in paraffine to  $250^\circ\text{C}$ ., it was found to be incapable of bending, and was as brittle as when cold. In fracture and general characteristics it closely resembled the bromide of silver.

Placed in the expansion-apparatus the bar expanded regularly up to  $125.5^\circ\text{C}$ ., and more rapidly than the chloride or bromide of silver; between  $125.5^\circ\text{C}$ . and  $131.5^\circ\text{C}$ . a slight contraction took place; at  $131.5^\circ\text{C}$ . the mass began to expand again, and it expanded more rapidly than the chloride or bromide; at the melting-point and at  $750^\circ\text{C}$ ., however, the volume was nearly the same as that of the bromide. The following results were obtained:—

*Coefficient of cubical expansion for 1° C.*

° C.	° C.	
Between 0	and 125·5	..... = ·00012216
„	125·5 and 131·5 (contraction)	..... = ·00004902
„	131·5 and fusing-point (330° C.)	..... = ·00015882
Expansion in passing from the solid to the liquid state		= ·057390
Between 330° C.	and 750° C.	..... = ·0001760

If we take the volume at 0° C. as unity we have—

	° C.	
Volume at	0	= 1·000000
„	125·5	= 1·015331
„	131·5	= 1·015037
„	330	= 1·046666 (solid)
„	330	= 1·104050 (liquid)
„	750	= 1·177979

The alloy clearly possesses two points of similar density at different temperatures, the one at 131°·5 C., the other at or about 123° C.

2. CHLORO-BROM-IODIDE OF SILVER HAVING THE COMPOSITION  $\text{Ag I Ag Br Ag Cl}$ , OR  $\text{Ag}_3 \text{I Br Cl}$ .

The alloy contains :—

Ag I . . .	41·484	Ag . . .	57·1932
Ag Br ..	33·186	I . . . .	21·4184
Ag Cl ..	25·330	Br . . . .	14·1218
		Cl . . . .	6·2666
	<hr/>		<hr/>
	100·000		100·0000

Specific gravity 6·1197. Calculated specific gravity on the assumption that no condensation takes place = 5·801, showing a condensation equal to ·0519 on the calculated volume. Fusing-point 295° C. Specific gravity of the liquid at the fusing-point = 5·5673; at 750° C. = 5·118. The mass fuses to a dark bromine-red liquid, becoming a solid of the same colour, which changes to a pink, dull opaque brick-red, and finally when the mass is cold to a dull orange. The powder is bright orange, becoming bright green on exposure to light. The fused mass on exposure to light becomes of a dark steel-grey colour. The mass is compact, hard, and homogeneous; it is semitransparent in thin layers. Semicrystalline fracture. Somewhat lustrous at the surface. Gives a clear metallic ring when allowed to fall on an anvil, or when short rods of the alloy are shaken together. It is difficult to break, and has more tenacity than any one of its constituents. It does not bend when cold; and taken from the paraffine-bath at 250° C. it bends slightly, but breaks easily.

In the expansion-apparatus the bar expanded as regularly but not quite so rapidly as the alloy No. 1. Up to  $124^{\circ}\text{C}$ . the coefficient of expansion is nearly the same as that of the bromide of silver. Between  $124^{\circ}\text{C}$ . and  $133^{\circ}\text{C}$ . it contracted more than the preceding; at  $133^{\circ}\text{C}$ . the rod began to expand again, and it expanded now both more than the bromide and more than alloy No. 1 during the same ranges of temperature. At the melting-point the volume is less than that of the bromide, however, and at  $750^{\circ}\text{C}$ . it is nearly the same.

The following results were obtained:—

*Coefficient of cubical expansion for 1° C.*

	$^{\circ}\text{C}$ .	$^{\circ}\text{C}$ .	
Between	0 and 100	.....	= $\cdot 00009529$
„	100 and 124	.....	= $\cdot 00010451$
„	124 and 133 (contraction)	.....	= $\cdot 00060000$
„	133 and fusing-point ( $295^{\circ}\text{C}$ .)	.....	= $\cdot 00020250$
Expansion in passing from the solid to the liquid state			= $\cdot 05084000$
Between	$295^{\circ}\text{C}$ . and $750^{\circ}\text{C}$ .	.....	= $\cdot 00016130$

It is curious and anomalous that the coefficient of expansion of the liquid between  $295^{\circ}\text{C}$ . and  $750^{\circ}\text{C}$ . should be less than that of the solid between  $133^{\circ}\text{C}$ . and  $295^{\circ}\text{C}$ .; but the results were concordant, and it must be noted that the expansion between  $133^{\circ}\text{C}$ . and  $295^{\circ}\text{C}$ . is nearly double that of the most expansible of metals. The coefficient between these limits appeared to decrease as the temperature rose; but as the mass, or at least one of its constituents, undergoes at  $133^{\circ}\text{C}$ . a molecular change, passing into an amorphous plastic condition, and as of necessity there is some strain on the rod, it was thought that this decrease of the coefficient might be due to increase of plasticity and consequent slight yielding of the bar; and the first determination (that is to say at the lowest temperature possible above  $133^{\circ}\text{C}$ .) was taken, and the above coefficient, which may consequently be somewhat too high, was deduced from it.

If we take the volume at  $0^{\circ}\text{C}$ . as unity we have—

	$^{\circ}\text{C}$ .	
Volume at	0	= 1.000000
„	100	= 1.009529
„	124	= 0.012037
„	133	= 1.006637
„	295	= 1.039442 (solid)
„	295	= 1.090280 (liquid)
„	750	= 1.163720

The alloy has two points of similar density at different temperatures, owing to the contraction which takes place between  $124^{\circ}$  and  $133^{\circ}\text{C}$ . The one temperature is  $133^{\circ}\text{C}$ ., the other at or about  $70^{\circ}\text{C}$ .

3. CHLORO-BROM-IODIDE OF SILVER HAVING THE COMPOSITION  $\text{Ag}_2\text{I}_2\text{AgBrAgCl}$ , OR  $\text{Ag}_4\text{I}_2\text{BrCl}$ .

The alloy contains:—

Ag I . . . .	58·6404	Ag . . . .	53·8989
Ag Br . .	23·4557	I . . . .	31·6905
Ag Cl . . . .	17·9039	Br . . . .	9·9813
		Cl . . . .	4·4293
<hr/>		<hr/>	
100·0000		100·0000	

Specific gravity 6·503; after annealing by slow cooling in paraffine 5·997. Calculated specific gravity on the assumption that no condensation takes place = 5·762, showing a condensation equal to ·0487 on the calculated volume. Fusing-point  $320^\circ\text{C}$ . Specific gravity of the liquid at the fusing-point = 5·6971; at  $750^\circ\text{C}$ . = 5·3749. Fused to a dark bromine-red liquid, which, after passing through the different changes of colour as No. 2 alloy, finally cooled to a dark orange-coloured opaque solid. Both the exterior of the fused mass and the bright orange-coloured powdered substance turned green on exposure to diffused light. The mass contracted on cooling. Taken from the paraffine-bath at  $250^\circ\text{C}$ . it was found to be flexible, and it could be bent through an angle of  $40^\circ$  before breaking; when somewhat cooler it was brittle and easily broken, but when cold it was tenacious and difficult to break. It was compact and homogeneous, and gave a clear metallic ring when allowed to fall on an anvil. In the expansion-apparatus the bar expanded regularly, but much less rapidly than Nos. 1 and 2, up to  $124^\circ\text{C}$ . Between  $124^\circ\text{C}$ . and  $133^\circ\text{C}$ . it contracted considerably more than No. 2 alloy; at  $133^\circ\text{C}$ . it began to expand, and between  $133^\circ\text{C}$ . and  $320^\circ\text{C}$ . it expanded at the same rate as No. 2. At the melting-point and at  $750^\circ\text{C}$ . the volume was less than that of either of the preceding.

The following results were obtained:—

*Coefficient of cubical expansion for  $1^\circ\text{C}$ .*

	$^\circ\text{C}$ .	$^\circ\text{C}$ .	
Between	0	and 124	..... = ·00008307
„	124	and 133 (contracting)	..... = ·00189999
„	133	and fusing-point ( $320^\circ\text{C}$ .)	..... = ·00020250
Expansion in passing from the solid to the liquid state			= ·02771500
Between $320^\circ\text{C}$ . and $750^\circ\text{C}$ .			..... = ·00012390

If we take the volume at  $0^\circ\text{C}$ . as unity we have—

Volume at	$^\circ\text{C}$ .	
	0	= 1·000000
„	124	= 1·010301
„	133	= ·993201
„	320	= 1·031068 (solid)
„	320	= 1·058783 (liquid)
„	750	= 1·112020

It will be seen that this alloy has two temperatures of maximum density or minimum volume, the one  $133^{\circ}\text{C.}$ , the other about  $-84^{\circ}\text{C.}$ , if we assume that the coefficient of expansion is the same between  $-100^{\circ}\text{C.}$  and  $0^{\circ}\text{C.}$  as it is between  $0^{\circ}\text{C.}$  and  $100^{\circ}\text{C.}$

4. CHLORO-BROM-IODIDE OF SILVER HAVING THE COMPOSITION  $\text{Ag}_3\text{I}_3\text{AgBrAgCl}$ , OR  $\text{Ag}_5\text{I}_3\text{BrCl}$ .

The alloy contains :—

Ag I . . . .	68.0171	Ag . . . .	52.0984
Ag Br . .	18.1379	I . . . . .	36.7583
Ag Cl . .	13.8450	Br . . . .	7.7183
		Cl . . . .	3.4250
<hr/>		<hr/>	
100.0000		100.0000	

Specific gravity 5.9717. Calculated specific gravity on the assumption that no condensation takes place = 5.741, showing a condensation equal to .0385 on the calculated volume. Fusing-point  $330^{\circ}\text{C.}$  Specific gravity of the liquid at the fusing-point = 5.643; at  $750^{\circ}\text{C.}$  = 5.333. Fused to a dark bromine-red liquid, and passed through the same changes of colour as alloy No. 3, finally cooled to a dull orange solid. Lustrous. Turned green on exposure to light. More brittle and less compact than the preceding. *Expanded* in cooling and broke the glass tube in which it was cast during the cooling, but not vigorously. A few longitudinal rifts appeared in the rod. At  $250^{\circ}\text{C.}$  sufficiently flexible to be bent through more than a right angle, but was brittle when cold. In the expansion-apparatus the bar expanded up to  $124^{\circ}\text{C.}$  to a less extent than the preceding; between  $124^{\circ}\text{C.}$  and  $133^{\circ}\text{C.}$  it contracted to a greater extent than the preceding; at  $133^{\circ}\text{C.}$  it commenced to expand again, and between  $130^{\circ}\text{C.}$  and  $330^{\circ}\text{C.}$  it expanded less than the preceding. At the melting-point and at  $750^{\circ}\text{C.}$  the volume was less than that of any of the preceding.

The following results were obtained :—

*Coefficient of cubical expansion for  $1^{\circ}\text{C.}$*

	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	
Between	0 and 124	.....	= .00006000
„	124 and 133 (contraction)	.....	= .00259998
„	133 and 330	.....	= .00011571
Expansion on passing from the solid to the liquid state			= .048033
Between $330^{\circ}\text{C.}$ and $750^{\circ}\text{C.}$		.....	= .00012359

If we take the volume at  $0^{\circ}\text{C.}$  as unity we have—

Volume at	$^{\circ}\text{C.}$	
	0	= 1.000000
„	124	= 1.007440
„	133	= .984041

	° C	
Volume at	330	= 1·006834 (solid)
„	330	= 1·054867 (liquid)
„	750	= 1·106782

This alloy, like the preceding, has obviously two temperatures of maximum density or minimum volume; the one 133° C., the other at some point far below zero.

5. CHLORO-BROM-IODIDE OF SILVER HAVING THE COMPOSITION  $\text{Ag}_4 \text{I}_4 \text{Ag Br Ag Cl}$ , OR  $\text{Ag}_6 \text{I}_4 \text{Br Cl}$ .

The alloy contains :—

Ag I . . . .	73·9285	Ag . . . .	50·9634
Ag Br . .	14·7856	I . . . . .	39·9528
Ag Cl . .	11·2859	Br . . . .	6·2919
		Cl . . . .	2·7919
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	100·0000		100·0000

Specific gravity = 5·907. Calculated specific gravity on the assumption that no condensation takes place = 5·725, showing a condensation equal 0·291 on the calculated volume. Fusing-point 350° C. Specific gravity of the liquid at the fusing-point = 5·680; at 750° C. = 5·340. Fuses to a bromine-red liquid, which cools to a mass of the same colour. As the mass cools it becomes bright brick-red, dull brick-red, orange-red, and finally, when cold, a rich orange-yellow. It turns green both in mass and in powder on exposure to light. It expands in solidifying, and cracks the tube in which it is cast as vigorously as the iodide of silver itself. It forms a brittle solid when cold, and possesses a number of horizontal rifts produced at the moment of expansion. More brittle than any of the preceding compounds, but less so than Ag I. Crystalline fracture. Lustrous surface. Harsh crystalline noises during cooling. Taken from the paraffine-bath at 250° C., it was so plastic that it could not only be bent upon itself, but twisted like a corkscrew. In the expansion-apparatus the bar expanded up to 124° C. to a less extent than the preceding; between 124° C. and 133° C. it contracted to a greater extent than the preceding; at 133° C. it commenced to expand again, and between 133° and 350° C. it expanded to a less extent than the preceding. At the melting-point and at 750° C. the volume was less than that of any of the preceding.

The following results were obtained :—

	<i>Coefficient of cubical expansion for 1° C.</i>	
	° C.	° C.
Between	0 and 124	·00005400
„	124 and 133 (contraction).	·00270000
„	133 and 350	·00010800
Expansion on passing from the solid to the liquid state.		·03414100
Between	350° and 750° C.	·00014379

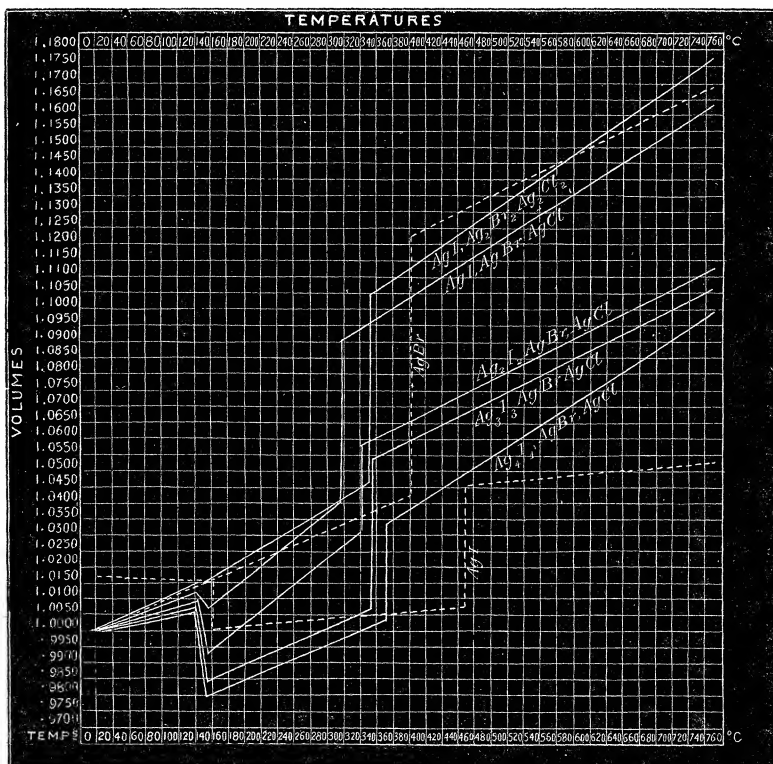


If we take the volume at  $0^{\circ}\text{C.}$  as unity we have—

Volume at	$^{\circ}\text{C.}$	
0	=	1.000000
124	=	1.006696
133	=	.979696
350	=	1.003132 (solid)
350	=	1.037273 (liquid)
750	=	1.094790

This alloy, like the preceding, has two temperatures of maximum density or minimum volume; the one at  $133^{\circ}\text{C.}$ , the other at some point far below zero.

*Table showing approximately the Action of Heat on some Chloro-brom-iodides of Silver, between  $0^{\circ}\text{C.}$  and  $750^{\circ}\text{C.}$*



The experimental results obtained with the last two alloys were less consonant than those of the other alloys, which might be predicted from the nature of the alloys in question.

GENERAL CONCLUSIONS.—There are several questions connected with the chloro-bromo-iodides of silver which require to be discussed, and it may be well to take them under separate headings.

*Comparison of the alloys with their constituents.*—For all purposes of these comparisons we may take the bromide and chloride of silver together, since their coefficients of expansion and certain other relations to heat are very much the same. It will be noticed that the first alloy contains only 26 per cent. iodide of silver, while the four succeeding alloys contain respectively 41, 58, 68, and 74 per cent. If we compare the percentage of silver we find :—No. 1, 60 per cent. ; No. 2, 57 ; No. 3, 54 ; No. 4, 52 ; and No. 5, 51 : or, again, in No. 1 we have 14 per cent. of iodine to 25 of Br and Cl ; in No. 2, 21 of I to 20 of Br and Cl ; in No. 3, 31 of I to 14 of Br and Cl ; in No. 4, 36 of I to 11 of Br and Cl ; and in No. 5, 40 of I to 8 of Br and Cl. The first alloy is scarcely affected at all as regards its coefficients of expansion by the presence of the iodide, and, in fact, resembles bromide of silver in all its properties ; on the other hand, the alloys Nos. 4 and 5 are very much affected by the presence of the large amount of iodide of silver they contain, and in many respects resemble the iodide. The greatest divergence from the properties of the constituents is to be found in the alloys Nos. 2 and 3, in which the iodide varies between 40 and 60 per cent. Perhaps this is due to the fact that the iodide only dissolves to a certain extent in the fused bromide and chloride ; for we notice that certain properties of the iodide are masked so long as the iodide does not exceed a certain percentage, while they become very apparent as the amount of iodide is increased.

*Of the point of maximum density of the alloys.*—While the bromide and chloride of silver expand regularly like any ordinary solid, it has been shown that the iodide contracts slightly up to  $142^{\circ}$  C., considerably between  $142^{\circ}$  C. and  $145^{\circ}5$  C., and that it possesses its point of maximum density at the latter temperature. Now nothing could possibly be more definite or decided than the behaviour of the alloys at the critical temperature at which contraction commences during the heating of the mass. In the case of the alloys Nos. 2, 3, 4, and 5, this contraction invariably commenced at  $124^{\circ}$  C., and invariably finished at  $133^{\circ}$  C. In the case of No. 1 alloy, in which the percentage of iodide of silver was smallest, the contraction began at  $125^{\circ}5$  C. ( $1^{\circ}5$  C. higher than the others). The action took place with great precision in every instance. Here, then, we have the curious fact that while the iodide of silver commences its considerable contraction (which occurs simultaneously with its passage from the brittle crystalline state into the plastic amorphous state) at  $142^{\circ}$  C. and finishes it at  $145^{\circ}5$  C., the chloro-brom-iodide alloys commence their contraction  $18^{\circ}$  C. lower, and end it  $12^{\circ}5$  C. lower. Thus in the iodide it is effected in the heating through  $3^{\circ}5$  C., while in the alloy it requires  $9^{\circ}$  C. We must remember that in the alloy the iodide passes into the amorphous condition while it is disseminated through the mass of the bromide and

chloride; and perhaps the same cause as that which lowers the fusing-point lowers also the point of maximum density.

*Fusing-point.*—While the fusing-point of iodide of silver has been estimated at  $450^{\circ}\text{C}$ ., of bromide at  $380^{\circ}\text{C}$ ., and of chloride at  $350^{\circ}\text{C}$ ., that of the alloys is lower than any of the constituents (except No. 5, which is the same as that of the lowest of its constituents, while it contains 74 per cent. of the constituent with the highest fusing-point, viz.  $450^{\circ}\text{C}$ .). Thus No. 1 melts at  $330^{\circ}\text{C}$ ., No. 2 at  $295^{\circ}\text{C}$ ., No. 3 at  $320^{\circ}\text{C}$ ., No. 4 at  $330^{\circ}\text{C}$ ., and No. 5 at  $350^{\circ}\text{C}$ . The most distinctive alloy, No. 2, melts at a temperature which is  $155^{\circ}\text{C}$ . below that of the iodide which constitutes 41.5 per cent. of the weight of the alloy,  $85^{\circ}\text{C}$ . below that of the bromide which constitutes 33 per cent. of the alloy, and  $55^{\circ}\text{C}$ . below that of the chloride which constitutes 25 per cent. of the alloy. Now it is well known that in the case of numerous alloys the fusing-point is lower than that of the mean fusing-points of the components; further, it is known that a mixture of the fused chlorides of sodium and potassium has a lower fusing-point than the mean of the constituent salts. Dr. Matthiessen says, "It is generally admitted that matter in the solid state exhibits excess of attraction over repulsion, whilst in the liquid state these forces are balanced; and in the gaseous state repulsion predominates over attraction." Let us assume that similar particles of matter attract each other more powerfully than dissimilar ones. It will then follow that the attraction subsisting between the particles of a mixture will be sooner overcome by repulsion than in the case of a homogeneous body: hence mixtures should fuse more readily than their constituents. We are at least reminded of the fact that certain perfectly inert bodies, when mixed with substances which decompose at a certain temperature, lower the temperature of decomposition.

*Of the contraction of the alloys between  $124^{\circ}\text{C}$ . and  $133^{\circ}\text{C}$ .*—It is a curious fact that until the percentage of iodide of silver in the alloy becomes considerable, the chief influence of the iodide seems to be exerted between that narrow range of temperature; and more than this, that so soon as the contraction is over, the mass undergoes far more rapid expansion than do any of its constituents when heated through the same range of temperature. It is further noticeable that the amount of contraction in some of the alloys exceeds that of the iodide itself, while we know that the other constituents possess high coefficients of expansion. This is all dependent, without doubt, upon the manner in which the iodide changes its condition within the mass of the alloy. Let us take the case of one of the intermediate alloys, say No. 3; in every 100 molecules between the temperatures of  $124^{\circ}\text{C}$ . and  $133^{\circ}\text{C}$ . we have 58 molecules undergoing somewhat rapid contraction, while 42 are undergoing expansion; at the same time other events are taking place within the mass, heat is disappearing as internal work, and is changing the crystalline into the amorphous iodide, converting an opaque, brittle,

highly crystalline body (I speak of the iodide *alone*, not of the alloy) into a transparent, plastic, denser body. What the precise function of the molecular motion which disappears can be it is difficult to assume, since in this case it not only changes the state of the body, but approximates its molecules.

*Of the texture, specific gravity, &c. of the alloys.*—It is noticeable that when the percentage of iodide of silver is small, the alloy is brittle while hot, and only slightly more tenacious than its constituents when cold (No. 1); as the percentage of iodide increases, the alloy becomes somewhat less brittle while hot, and considerably more tenacious, hard, and compact, than any of its constituents (Nos. 2 & 3); while when the percentage of iodide becomes considerable (Nos. 4 & 5), the mass becomes extremely plastic while hot, perhaps more so than the iodide itself, and very brittle when cold. The specific gravity is in all cases *above* the mean of that of the constituents; it may be because the intercrystalline spaces of the iodide are now filled with bromide and chloride. Thus, while the sp. gr. of Ag Cl is 5.505, of Ag Br 6.245, and of Ag I 5.675, that of the alloys is as follows:—No. 1, 6.152; No. 2, 6.1197; No. 3, 6.503; No. 4, 5.9717; and No. 5, 5.907: while the percentage of the bromide, which alone has a higher specific gravity than that of the alloys, in no case exceeds 42.

In the accompanying curve table (p. 300) the expansion-curves of the iodide and bromide of silver have been added for comparison with those of the alloys; the curve of chloride of silver has been omitted, because it is almost precisely the same as that of the bromide.

I have preferred to call these results “approximate” on account of certain experimental difficulties in the way of very precise determinations, which difficulties I at present see no way of avoiding.

November 16, 1876.

Dr. J. DALTON HOOKER, C.B., President, in the Chair.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair.

Dr. Henry Edward Armstrong and Capt. George Strong Nares were admitted into the Society.

Prof. W. G. Adams, Mr. Bramwell, Mr. Busk, Dr. Russell, and General  
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Table showing approximately the Action of Heat on some Chloro-brom-  
isotiles of Silver, between  $0^{\circ}\text{C.}$  and  $750^{\circ}\text{C.}$

